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New complexes of platinum(0) with cyclopropenes*

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New cyclopropene complexes of platinum have been synthesised with a variety of bulky substituents on all positions of the cyclopropene ring. Two of these novel complexes, $[Pt(3,3\text{-}Ph_3C_3H_2)(PPh_3)_2]$ and $[Pt(1,2\text{-}Ph_2C_3H_2)(PPh_3)_2]$, have been structurally characterised by X-ray analysis. Both contain a cyclopropene ring which has remained intact upon complexation. The bond lengths within the complexes are remarkably independent of the substituents. The structural characteristics and the ^{31}P NMR spectra of these complexes are discussed in detail.

Cyclopropene is one of a series of alternative nitrogenase substrates the reduction of which might be expected to yield information about the structure and function of the nitrogenase reactive site. Now that the structures of classical molybdenum nitrogenases are reasonably well established,[1] it is evident that the 'active site' is not an obvious entity.[2] Indeed it is likely to consist of several metal atoms working in conjunction. It is also becoming clear that the reductions of substrates by nitrogenases may be very complex, involving as they do many electrons and protons, and also not necessarily occurring at the site at which dinitrogen is itself reduced.

There is no report of studies of the interaction of cyclopropenes with metal ions that can be used convincingly as models for nitrogenase reactivity. If we assume that cyclopropene first forms a complex with a metal ion and that this ligand then accepts both protons from solution and electrons from the metal ion, as has been proposed in the widely accepted models for dinitrogen reduction by nitrogenase,[3] then one would exclude from a first consideration all those cases where cyclopropene reacts with a metal complex, for example, with ring opening, before any possible reaction with protons and electrons could take place. Therefore we ignored the quite extensive chemistry of cyclopropenes with titanium, zirconium, tungsten, ruthenium, iridium and palladium,[4] and concentrated initially upon systems in which the cyclopropene ring remains intact upon reaction with the metal complex. The only previous attempt to use such complexes as models was with $[Nb(C_3H_4)(C_5H_5)_2]$, the spectroscopically characterised product obtained from $[NbCl_2(C_5H_5)_2]$, cyclopropene and sodium. It reacts with HCl to yield only cyclopropane as a hydrocarbon product.[5]

The number of proven, stable complexes of cyclopropenes is very small and is limited mainly to Group 10 metals. Many of the early transition metals form ring-opened products such as vinylalkylidene[6] complexes and metallacyclobutenes[7] upon reaction with cyclopropene, although ring-intact complexes have been invoked as intermediates in many cases. For example, $[Ni(C_2H_4)(PPh_3)_2]$ forms a nickelacyclopentane complex, bis(triphenylphosphine)-5-nickela-3,3,7,7-tetramethyl-*trans*-tricyclo[4.1.0.0]heptane, upon reaction with 2 mol equivalents of 3,3-dimethylcyclopropane.[8] However, when the methyl substituents are on the double bond, as in $1,3,3\text{-}Me_3C_3H$ and in C_3Me_4, an η^2 ring-intact complex is formed.[9] No ring-intact stable complex of palladium exists, but there is a series of complexes of platinum(0) of the form $[PtL(PPh_3)_2]$ (L = C_3H_4, $3\text{-}MeC_3H_3$, $3,3\text{-}Me_2C_3H_2$, $1,2\text{-}Me_2C_3H_2$, $1,3,3\text{-}Me_3C_3H$ or $1,2,3\text{-}Me_3C_3H$).[10] The structures of the second and fourth were determined by X-ray analysis.[11,12]

The influence of substituents on the reactions of the cyclopropene ring which is evident in nickel chemistry is also apparent in platinum chemistry. For example, $[Pt(C_2H_4)(PPh_3)_2]$ reacts with C_3F_4 to form a metallacyclobutene complex.[13] This has been ascribed to the different reactivity of carbon–fluorine bonds as compared to carbon–hydrogen bonds, whereas in the case of nickel the difference was ascribed to steric influences.[9]

In this paper we report on platinum complexes with a wider range of cyclopropenes, including those with bulky substituents at various positions of the cyclopropene ring. We wished to know whether these would influence the kind of complex formed. The reactions of new cyclopropene complexes with HCl will be described later. There are no ^{31}P NMR data in the literature for the known platinum–cyclopropene complexes, and this particular technique was very important for our product characterisation.

Results and Discussion

The work described in the literature[10–12] was restricted to methylcyclopropene derivatives and therefore we have extended the series of platinum(0) complexes to those with phenyl and bulkier substituents. They were obtained by the standard reaction of 1.5 equivalents of the cyclopropene with $[Pt(C_2H_4)(PPh_3)_2]$ in tetrahydrofuran (thf). *In situ* reduction of $[PtCl_2(dppe)]$ [dppe = 1,2-bis(diphenylphosphino)ethane] with sodium naphthalene in thf, followed by bubbling ethene through the solution, was necessary to form the unstable precursor complex, $[Pt(C_2H_4)(dppe)]$.[14]

In many cases the product was identified by its ^1H and ^{31}P NMR spectra. However, the structures of two new complexes were determined by X-ray structure analysis.† These have two phenyl residues attached to the cyclopropene ring, at the 3,3- and 1,2-positions, respectively. The structures of the corresponding complexes (3,3-diphenylcyclopropene)bis(triphenylphosphine)platinum(0) **1** and (1,2-diphenylcyclopropene)bis(triphenylphosphine)platinum(0) **2** are shown in Figs. 1 and 2, and selected bond lengths and angles are given in Tables 1 and 2. These two complexes were chosen to determine the effects on the corresponding complex of changing the position of bulky substituents on cyclopropene. In fact, ring-intact products were formed by both disubstituted cyclopropenes.

* *Non-SI unit employed*: mmHg ≈ 133.322 Pa.

† Previously reported briefly in ref. 4.

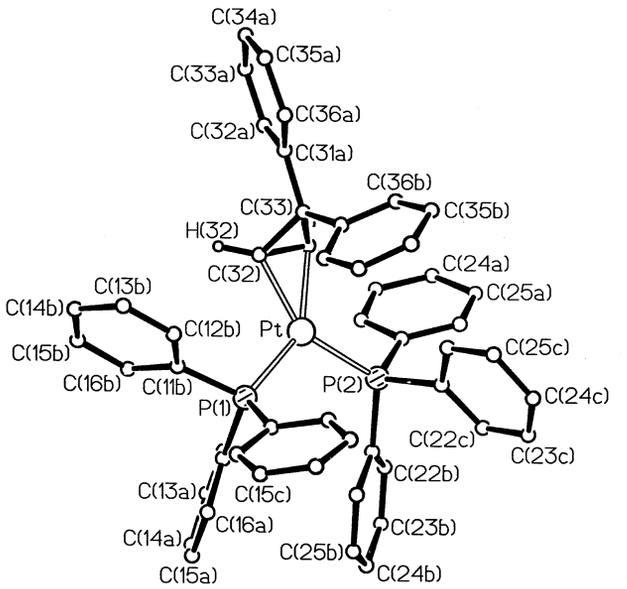

Fig. 1 Representation of the structure of $[Pt(3,3\text{-}Ph_2C_3H_2)(PPh_3)_2]$ **1** with numbering scheme

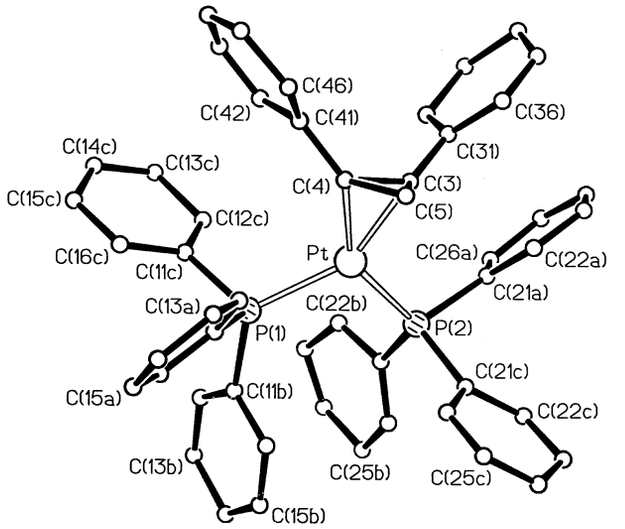

Fig. 2 Representation of the structure of $[Pt(1,2\text{-}Ph_2C_3H_2)(PPh_3)_2]$ **2** with numbering scheme

Table 1 Selected molecular dimensions in $[Pt(3,3\text{-}C_3H_2Ph_2)(PPh_3)_2]$ **1**. Bond lengths in Å, angles in °, estimated standard derivations (e.s.d.s) in parentheses

(a) About the Pt atom

Pt–P(1)	2.278(3)	Pt–C(31)	2.085(12)
Pt–P(2)	2.284(2)	Pt–C(32)	2.053(11)
P(1)–Pt–P(2)	108.8(1)	P(1)–Pt–C(32)	104.4(3)
P(1)–Pt–C(31)	144.7(2)	P(2)–Pt–C(32)	146.7(3)
P(2)–Pt–C(31)	106.1(2)	C(31)–Pt–C(32)	40.6(3)

(b) In the cyclopropene ligand

C(31)–C(32)	1.434(12)		
C(31)–C(33)	1.511(12)	C(32)–C(33)	1.519(11)
C(31)–H(31)	0.98(6)	C(32)–H(32)	0.979(25)
Pt–C(31)–H(31)	136(3)	C(32)–C(31)–C(33)	62.0(6)
Pt–C(32)–C(31)	70.9(6)	C(31)–C(33)–C(31b)	121.0(9)
Pt–C(31)–C(33)	104.5(7)	C(32)–C(33)–C(31a)	114.3(7)
H(32)–C(32)–C(33)	124(4)	Pt–C(31)–C(32)	68.5(6)
C(31)–C(33)–C(32)	56.5(5)	C(31)–C(32)–H(32)	139(4)
C(32)–C(33)–C(31b)	122.2(10)	H(31)–C(31)–C(33)	119(3)
Pt–C(32)–H(32)	130(4)	C(31)–C(32)–C(33)	61.5(6)
H(31)–C(31)–C(32)	126.7(27)	C(31)–C(33)–C(31a)	117.8(9)
Pt–C(32)–C(33)	105.7(6)	C(31a)–C(33)–C(31b)	113.6(8)

Table 2 Selected molecular dimensions in $[Pt(1,2\text{-}C_3H_2Ph_2)(PPh_3)_2]$ **2**. Bond lengths in Å, angles in °, e.s.d.s in parentheses

(a) About the platinum atom

Pt–P(1)	2.273(7)	Pt–C(3)	2.094(25)
Pt–P(2)	2.270(4)	Pt–C(4)	2.121(22)
P(1)–Pt–P(2)	106.0(2)	P(1)–Pt–C(4)	106.9(7)
P(1)–Pt–C(3)	147.5(7)	P(2)–Pt–C(4)	147.0(6)
P(2)–Pt–C(3)	106.4(7)	C(3)–Pt–C(4)	40.9(10)

(b) In the cyclopropene ligand

C(3)–C(4)	1.47(4)		
C(3)–C(31)	1.41(5)	C(4)–C(41)	1.47(3)
C(3)–C(5)	1.54(4)	C(4)–C(5)	1.50(3)
Pt–C(3)–C(31)	130.8(19)	Pt–C(4)–C(3)	68.6(12)
Pt–C(3)–C(4)	70.5(14)	Pt–C(4)–C(41)	129.8(17)
C(31)–C(3)–C(4)	134.2(24)	C(3)–C(4)–C(41)	123.6(28)
Pt–C(3)–C(5)	98.7(20)	Pt–C(4)–C(5)	98.9(15)
C(31)–C(3)–C(5)	130.3(21)	C(3)–C(4)–C(5)	62.5(17)
C(4)–C(3)–C(5)	59.6(18)	C(41)–C(4)–C(5)	130.8(21)
C(3)–C(5)–C(4)	57.8(16)		

As might be expected, the C=C bond lengths increase upon complexation. This bond length in free 3,3-dimethylcyclopropene is 1.294(10) Å [15] and increases to 1.434(12) Å in **1** and to 1.47(4) Å in **2**. The similarity between these complexed bond lengths is unexpected. In the analogous 1,2-dimethylcyclopropene platinum complex the corresponding bond length is 1.50(1) Å[10,12] but no precise figure has been given for the 3-monomethyl compound. Clearly there is considerable stretching of the double bond upon complexation to platinum, and the bond length is now more typical of a cyclopropane carbon–carbon single bond. In cyclopropane itself the carbon–carbon bond length is 1.510(2) Å.[15] The separation of the Pt from the third carbon atom of the cyclopropenyl ring is *ca.* 2.82 Å, and consequently there is no interaction between them. The protons on C(31) and C(32) of $[Pt(3,3\text{-}Ph_2C_3H_2)(PPh_3)_2]$ **1** were located and refined with constrained C–H distances (0.98 Å).

The bond angles in the new complexes are also more typical of cyclopropanes than cyclopropenes as the unique angle of the cyclopropene isosceles triangle increases from *ca.* 50° in the free cyclopropene to *ca.* 60° in the complexes.[15] The relief of ring strain in the small ring upon complexation may therefore provide some of the driving force for the ethene displacement from platinum. Upon complexation, the substituents at the double bond of the cyclopropene ring are bent away from the plane of the ring. This effect is less in **2**, the angles between the normals to the mean-plane of the RC=CR groups [R is H in **1** and C(Ph) in **2**] and the C_3 ring plane being 72.1° in **1** and 59.1° in **2**. However the cyclopropene ring is tilted more sharply away from the PtC_2 plane in **2**; the angles between the normals are 59.1° in **1** *vs.* 66.9° in **2**, and this tends to keep the bulky substituents further from the platinum.

The Pt–P bonds do not vary much from compound to compound, the values for all four solved complexes averaging 2.274(6) Å.[12] A survey of Pt–P bond lengths in a series of complexes of the general formula $[Pt(un)(PPh_3)_2]$ where 'un' is an unsaturated species such as an alkene showed the average Pt–P bond length to be 2.28 Å.[16] The Pt–C bond lengths are also very similar throughout the four characterised compounds. The formal square-planar co-ordination about the platinum is slightly distorted. The angle between the normals to the PtPP plane and the PtCC plane is 5.1° for **1** and 6.6° for **2**, and this compares with only 1.6° in $[Pt(C_2H_4)(PPh_3)_2]$.[17]

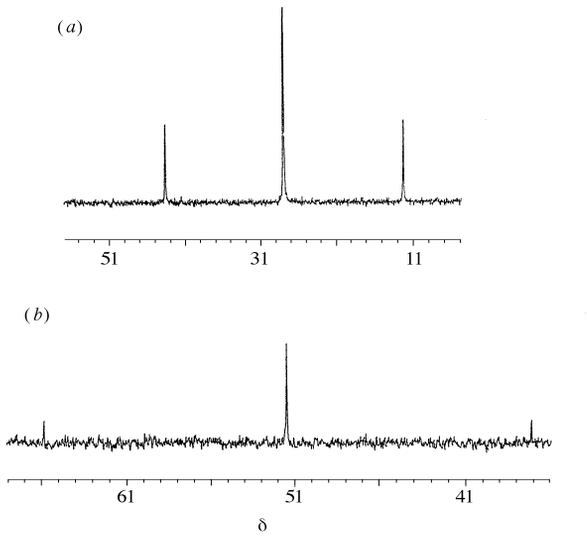

Fig. 3 Phosphorus-31 NMR spectra of (*a*) [Pt(3,3-$Ph_2C_3H_2$)(PPh_3)$_2$] **1** and (*b*) [Pt(3,3-$Ph_2C_3H_2$)(dppe)]

A feature of interest in these structures is the unsymmetrical nature of the metal–olefin bond. One might expect that a line dropped from the platinum atom to the mid-point of the carbon–carbon double bond should make a right angle with it, unless the substituents on the carbon atoms are electronically and/or sterically different. Any resulting asymmetry has been termed slippage,[18] and is measured by the distance from this intersection to the midpoint of the double bond. In complexes **1** and **2** the slippage is 0.046 and 0.037 Å, respectively. This is not negligible by comparison with previous examples, and the origin is far from obvious. It cannot be due to differences in substituents, as cited for earlier cases. Slippage has been suggested to be a measure of the susceptibility of the double bond to nucleophilic attack,[18] but we have no evidence on this point.

The ^{1}H NMR data for the complexes are summarised in the Experimental section. The most notable features are the large shielding of the protons at C(1) and C(2) of the cyclopropene ligand and the pronounced difference in chemical shifts of the *syn* and *anti* substituents on C(3). The large upfield shifts of the protons on C(1) and C(2) arise from their proximity to platinum and the change from a cyclopropene environment, with its associated deshielding effect, to a cyclopropane environment where the hybridisation of the attached carbon has changed from sp^2 to sp^3. The ^{1}H NMR spectra of such complexes have been analysed by Visser *et al.*[11] The ^{195}Pt chemical shifts are typical of four-co-ordinate platinum(0) compounds.[19]

Table 3 summarises the ^{31}P NMR data for the complexes prepared in this study. The range of chemical shifts is quite small and is characteristic of Pt^0 complexes. Cyclopropenes with different substituents at the double bond give rise to complexes with non-equivalent phosphorus atoms, as would be expected. The chemical shifts of the dppe complexes are significantly downfield of those of the PPh_3 complexes (see Fig. 3). This may be due to ring strain in the five-membered chelate ring.[20]

The $^1J_{PtP}$ coupling constants listed are indicative of the oxidation state of the metal and s character in the platinum–phosphorus bonds.[21] As the amount of s character in the bond increases, so also does the value of $^1J_{PtP}$. The observed values are quite large, as expected of Pt^0 complexes with few ligands. The values of $^1J_{PtP}$ for the dppe complexes are smaller than those of the analogous PPh_3 complexes by *ca.* 170–360 Hz. This implies better overlap of phosphorus and platinum orbitals in PPh_3 complexes. The overlap should increase as the bond angle P–Pt–P approaches 109°.[22] The bond angle P–Pt–P in dppe complexes is *ca.* 85° compared to *ca.* 107° in PPh_3 complexes,[23] entirely consistent with the lesser s character in the bond and the lower value of $^1J_{PtP}$.

Table 3 Phosphorus-31 NMR data for novel platinum–cyclopropene complexes

L in [Pt(L)(PPh_3)$_2$]	Solvent	δ	$^1J_{PtP}$/Hz
C_2H_4	CD_2Cl_2	33.6	3755
3,3-$Ph_2C_3H_2$	$CHCl_3$	27.9	3436
1,2-$Ph_2C_3H_2$	CD_2Cl_2	30.3	3384
3,3-$Me_2C_3H_2$	$CDCl_3$	33.5	3390
3-Me-3-PhC_3H_2	$CDCl_3$	32.9	3452
1.2-$Bu_2C_3H_2$	$CDCl_3$	30.3	3289
1-Bu-2-$Me_3SiC_3H_2$*	$CHCl_3$	28.8	3504
C_3H_4	$C_6H_5CH_3$	32.2	3373
L in [PtL(dppe)]			
C_2H_4	thf	54.9	3305
3,3-$Ph_2C_3H_2$	thf	51.5	3147
1,2-$Ph_2C_3H_2$	thf	50.6	3035
3,3-$Me_2C_3H_2$	thf	54.5	3046
3-Me-3-PhC_3H_2	thf	54.7	3119
1,2-$Bu_2C_3H_2$	thf	52.5	2961

* $^2J_{PP}$ = 38 Hz.

There were only two cyclopropenes investigated that did not form η^2 adducts. 1,2,3-Tri-*tert*-butylcyclopropene did not react with [Pt(C_2H_4)(PPh_3)$_2$], presumably due to the bulky butyl groups, and 3-chloromethyl-1,2-dichloro-3-methylcyclopropene appeared to undergo oxidative addition across one of the carbon–carbon bonds, with the formation of a Pt–Cl bond. The ^{31}P NMR spectrum showed that the phosphorus atoms are in two different environments implying a *cis* geometry for the complex. A large $^1J_{PtP}$ value (4250 Hz) also implies that one of the PPh_3 groups is probably *trans* to a chloride atom. The CH_2Cl group appears to be retained, so that the oxidative addition has apparently involved a chlorine originally at the double bond of the cyclopropene ring. The likely formulation for the complex is thus *cis*-[Pt{$C_3MeCl(CH_2Cl)$}Cl(PPh_3)$_2$]. There was no indication of the formation of an intermediate η^2 complex. Similar platinum chemistry with dihalogenated alkenes has been reported,[24] though in that case the intermediate η^2 complex was isolated.

Experimental

Solvents were dried and distilled under dinitrogen and standard Schlenk and syringe techniques were routinely used. 1,2-Diphenylcyclopropene was used as supplied by Aldrich Chemical Co. and K_2[$PtCl_4$] was used as supplied by Johnson Matthey plc. Cyclopropene was a gift from Professor C. E. McKenna (University of Southern California, Los Angeles), 1-butyl-1,2,2-tribromocyclopropane was kindly donated by Professor M. Baird (University College of North Wales, Bangor) and 1,2,3-tri-*tert*-butylcyclopropene was donated by Professor F. G. N. Cloke (University of Sussex). The following compounds were prepared by literature methods: 1,2-diphenylcyclopropene,[25] 3-chloromethyl-1,2-dichloro-3-methylcyclopropene,[26] *cis*-[$PtCl_2$(PPh_3)$_2$],[27] [Pt(C_2H_4)(PPh_3)$_2$],[27] [$PtCl_2$(dppe)][22] {particular care must be taken in this preparation as [Pt(dppe)$_2$]Cl_2 is formed easily under the same conditions},[28] [Pt(C_2H_4)(dppe)],[14] [Pt(3,3-$Me_2C_3H_2$)(PPh_3)$_2$][11] and [Pt(C_3H_4)(PPh_3)$_2$].[11]

The NMR spectra were recorded on a JEOL GSX-270 spectrometer using the solvent as reference for ^{1}H NMR spectra and the values quoted are upfield from $SiMe_4$; H_3PO_4–C_6D_6 was used as the external reference for ^{31}P NMR spectra. The ^{195}Pt NMR spectra were recorded at the University of Sussex on a Bruker AMX-500 spectrometer and were referenced to [$PtCl_6$]$^{2-}$. All reported chemical shifts are in ppm, and coupling constants are in Hz. Elemental analysis was carried out at the University of Surrey and also by Butterworth Laboratories. Electron impact (EI) mass spectral analyses were carried out

on a Fisons VG Autospec with an EI source at 70 eV (≈1.1215 × 10^{-17} J).

Preparations

3,3-Diphenylcyclopropene. (*a*) 1,1-*Dibromo*-2,2-*diphenylcyclopropane*. A two-necked 500 cm^3 round-bottomed flask was equipped with a pressure-equalising dropping funnel and a mechanical stirrer, KOBu^t (24.2 g, 220 mmol) was placed in the flask and 1,1-diphenylethene (100 g, 550 mmol) was added *via* the funnel over 1 h. A change from orange to brown was observed. The apparatus was cooled to 0 °C and bromoform (15 cm^3, 1.72 mol) added over 1 h. Work-up consisted of the addition of dichloromethane (200 cm^3) followed by water (100 cm^3). The organic layer was separated and washed with water several times. The aqueous layer was washed with dichloromethane and the washings added to the primary organic layer. The organic layer was evaporated to dryness giving a tan solid which was filtered off. Upon washing with cold hexane (2 × 20 cm^3) the tan colour was lost leaving a white product, yield 44.4 g (23%). ^{1}H NMR (CD_2Cl_2): δ 1.76 (s, 2 H, CH_2) and 7.44–7.8 (m, 10 H, C_6H_5) (Found: C, 51.1; H, 3.2. $C_{15}H_{12}Br_2$ requires: C, 51.1; H, 3.4%). Mass spectrometry: *m*/*z* 352 (M^+, 7), 271 (M − Br, 50), 191 (M − 2Br, 100), 166 (CPh_2, 46) and 115 (C_3H_2Ph, 16%).

(*b*) 1-*Bromo*-2,2-*diphenylcyclopropane*. The product from (*a*) (24 g, 68.2 mmol) was dissolved in a minimum amount of dichloromethane in a 250 cm^3 round-bottomed flask. The apparatus was cooled to 0 °C and Bu_3SnH (20 g, 68.8 mmol) was added *via* a pressure-equalising dropping funnel over 30 min. The flask contents were warmed to room temperature and stirred for 1 h. The reaction mixture was concentrated until precipitation occurred. The product was filtered off and washed with cold hexane (50 cm^3) to yield a white crystalline product, yield 12.1 g (65%). ^{1}H NMR (CD_2Cl_2): δ 1.81, 1.86 (2 dd, 2 H, $^2J_{H^aH^b}$ = 6.42, $^3J_{H^aH^x}$ = 7.92, $^3J_{H^bH^x}$ = 6.62, CH_2), 3.67 (dd, 1 H, CHBr) and 7.15–7.44 (m, 10 H, C_6H_5). Mass spectrometry: *m*/*z* 193 (M^+ − Br, 100), 178 (M − Br − CH_2, 70), 165 (CPh_2, 77), 115 (C_3H_2Ph, 93) and 77 (Ph, 32%).

(*c*) 3,3-*Diphenylcyclopropene*. The product from (*b*) (3.0 g, 11.0 mmol) and KOBu^t (2.24 g, 20.1 mmol) were placed in a 100 cm^3 round-bottomed flask under dinitrogen. Dimethyl sulfoxide (dmso) (10 cm^3) was added while stirring. The solution started to turn green. The flask was heated to 50–55 °C and left for 16 h and the contents turned brown. The flask was allowed to cool and hexane (15 cm^3) was added. A small amount of white precipitate resulted and this was filtered off and discarded. Water (20 cm^3) was added to the filtrate and two layers formed. The deep yellow organic layer was washed with water. The aqueous layer was washed with hexane (3 × 20 cm^3) and the washings added to the primary organic layer. The organic layer was dried over anhydrous sodium sulfate, filtered and then taken to dryness *in vacuo*. Note that the dmso must be dry to prevent formation of 1,1-diphenylcyclopropane, yield 1.77 g (84%). ^{1}H NMR [$(CD_3)_2SO$]: δ 7.92 (s, 2 H, CH=CH) and 7.07–7.3 (m, 10 H, C_6H_5).

3,3-Dimethylcyclopropene.[29] (*a*) 1,1-*Dibromo*-2,2-*dimethylcyclopropane*. A three-necked 500 cm^3 round-bottomed flask was equipped with a pressure-equalising dropping funnel, a mechanical stirrer and a gas inlet under dinitrogen, KOBu^t (140 g, 125 mmol) was placed in the flask and 2-methylpropene (200 g, 356 mmol) was condensed over 2 h into the vessel which had been cooled to −60 °C. The apparatus was allowed to warm to −30 °C and bromoform (85 cm^3, 970 mmol) was added over 1.5 h. The extraction was as described for the diphenyl compound and the product was isolated by distillation. The product is a colourless liquid which distils at 47–48 °C at 10^{-3} mmHg, yield 156 g (70%). ^{1}H NMR ($CDCl_3$): δ 1.36 (s, 6 H, CH_3) and 1.4 (s, 2 H, CH_2).

(*b*) 1-*Bromo*-2,2-*dimethylcyclopropane*. 1,1-Dibromo-2,2-dimethylcyclopropane (39.0 g, 171 mmol) was placed in a two-necked flask equipped with a pressure-equalising dropping funnel and distillation condenser. The apparatus was cooled to 0 °C and Bu_3SnH (50 g, 172 mmol) was added *via* the funnel during 30 min. The solution was allowed to warm to room temperature while stirring for 1 h. The contents of the flask were distilled at atmospheric pressure and the fraction boiling at 102–104 °C was collected, yield 19.7 g (77%). ^{1}H NMR ($CDCl_3$): δ 0.61 (dd, 1 H, $^2J_{H^aH^b}$ = 6.04, $^3J_{H^aH^x}$ = 9.36, H^a), 0.94 (dd, 1 H, $^3J_{H^bH^x}$ = 5.87, H^b), 1.09 (s, 3 H, CH_3), 1.23 (s, 3 H, CH_3) and 2.79 (dd, 1 H, H^x).

(*c*) 3,3-*Dimethylcyclopropene*. A two-necked flask with a pressure-equalising dropping funnel and a Schlenk vessel in a liquid-nitrogen trap to collect the product was used under vacuum as a flash distillation apparatus. Dimethyl sulfoxide (40 cm^3) and KOBu^t (13.8 g, 123 mmol) were placed in the flask. The apparatus was heated to 100 °C and 1-bromo-2,2-dimethylcyclopropane (19 g, 127 mmol) was added *via* the funnel over 2 h. The contents of the flask were held for 5 h at 100 °C. The product was collected in the cold Schlenk vessel as a colourless liquid, yield 5.3 g (61%). ^{1}H NMR (C_7D_8): δ 1.15 (s, 6 H, CH_3) and 7.17 (s, 2 H, CH=CH).

3-Methyl-3-phenylcyclopropene.[30] (*a*) 1,1-*Dibromo*-2-*methyl*-2-*phenylcyclopropane*. α-Methylstyrene (103 g, 870 mmol) and KOBu^t (16.8 g, 149 mmol) were placed in a 500 cm^3 flask under dinitrogen and the flask was then cooled to between −5 and −10 °C. Bromoform (36.8 g, 146 mmol) was added from a pressure-equalising dropping funnel during 1 h. The flask was kept at −5 °C for 3 h and then held for 36 h at 5 °C. Water (200 cm^3) and an aliquot of HCl was added. The organic layer was extracted with hexane which was subsequently evaporated off. The product was obtained as a viscous colourless liquid by distillation at 120 °C at 10^{-3} mmHg. It solidifies at room temperature if very pure, yield 24.3 g (57%). ^{1}H NMR ($CDCl_3$): δ 1.69 (s, 3 H, CH_3), 1.76 (d, 1 H, $^2J_{H^aH^b}$ = 7.51, H^a), 2.15 (d, 1 H, H^b) and 7.23–7.34 (m, 5 H, C_6H_5).

(*b*) 1-*Bromo*-2-*methyl*-2-*phenylcyclopropane*. 1,1-Dibromo-2-methyl-2-phenylcyclopropane (10.5 g, 36.2 mmol) was heated in a flask to 45 °C and Bu_3SnH (9.82 g, 33.7 mmol) was added over 20 min *via* a pressure-equalising dropping funnel. The contents of the flask were stirred for 48 h at room temperature. Distillation at 10^{-3} mmHg yielded the pure product at 100–104 °C, yield 3.6 g (51%). ^{1}H NMR (CDl_3) (2 geometric isomers present, coupling constants not determined): δ 1.05 (2 dd, 2 H, H^a of both isomers), 1.32 (2 dd, 2 H, H^b of both isomers), 1.59 (s, 6 H, $2CH_3$) 3.07 (dd, 1 H, H^x of one isomer), 3.21 (dd, 1 H, H^x of one isomer) and 7.16–7.30 (m, 10 H, C_6H_5).

(*c*) 3-*Methyl*-3-*phenylcyclopropene*. A flash distillation apparatus containing KOBu^t (1.3 g, 11.6 mmol) and dmso (10 cm^3) was placed under a slight vacuum and 1-bromo-2-methyl-2-phenylcyclopropane isomeric mixture (1.8 g, 8.5 mmol) was added *via* syringe. The reaction solution was stirred for 4 h at room temperature under vacuum with the receiving flask cooled in a liquid nitrogen bath. The product, contaminated with some dmso, was collected and the dmso removed by elution with diethyl ether on an Al_2O_3 column. The diethyl ether was removed under a stream of dinitrogen. ^{1}H NMR ($CDCl_3$): δ 1.6 (t, 3 H, $^4J_{HH}$ = 0.73, CH_3) and 7.0–7.18 (m, 7 H, C_6H_5 and CH=CH).

1,2-Dibutylcyclopropene. 1-Butyl-1,2,2-tribromocyclopropane (3.0 g, 9.0 mmol) was dissolved in diethyl ether (10 cm^3) under dinitrogen. The solution was cooled to −80 °C and LiBu (12.3 cm^3, 1.6 mol dm^{-3} in hexane) was added. The mixture was allowed to come to room temperature and then stirred for 1 h. Iodobutane (1.2 cm^3, 10.5 mmol) and hmpa (hexamethylphosphoramide, 3.2 cm^3, 18.4 mmol) were added at 0 °C and the reaction mixture was stirred overnight at room temperature. Water (10 cm^3) was added and the aqueous layer was washed

with diethyl ether (4 × 20 cm^3), the washings combined with the ether layer and subsequently washed with water. The ether was removed *in vacuo*. A flash distillation removed all side-products leaving a clean yellow oil, yield 0.95 g (69%). ^{1}H NMR ($CDCl_3$): δ 0.82 (s, 2 H, CH_2), 0.95 (t, 6 H, CH_3 of butyl), 1.45, 1.6 (m, 8 H, β-CH_2 and γ-CH_2 of butyl) and 2.39 (t, 4 H, α-CH_2 of butyl).

1-Butyl-2-trimethylsilylcyclopropene. The method was as used for the preparation of 1,2-dibutylcyclopropane except that LiMe (15 cm^3, 1.4 mol dm^3 solution in hexane) was used instead of LiBu–hmpa and Me_2SiI (2.16 g, 10.8 mmol) was added instead of BuI to 1-butyl-1,2,2-tribromocyclopropane (3.0 g, 9.0 mmol), yield 0.74 g (49%). ^{1}H NMR ($CDCl_3$): δ −0.05 (s, 9 H, $SiMe_3$), 0.55 (s, 2 H, CH_2), 0.75 (t, 3 H, CH_3 of butyl), 1.05–1.5 (m, 4 H, CH_2CH_2 of butyl) and 2.4 (t, 2 H, α-CH_2 of butyl).

(3,3-Diphenylcyclopropene)bis(triphenylphosphine)platinum 1. To [$Pt(C_2H_4)(PPh_3)_2$] (0.40 g, 0.53 mmol) dissolved in thf (15 cm^3) under nitrogen was added 3,3-diphenylcyclopropene (0.15 g, 0.78 mmol) *via* syringe. The reaction mixture was stirred for 20 min. Ethanol (60 cm^3) was added and the volume was reduced under a stream of dinitrogen with gentle heating on a water bath until precipitation occurred. The precipitate was collected by filtration and washed with ether. A second crop was formed upon storing the mother-liquor at −20 °C. Recrystallisation was from toluene and ethanol, yield 0.45 g (93%). ^{1}H NMR ($CDCl_3$): δ 3.06 (tt, 2 H, $^3J_{PH}$ = 7.2, $^2J_{PtH}$ = 18.4, CH=CH) and 6.95–7.65 (m, 40 H, C_6H_5). Mass spectrometry: *m*/*z* 912 (*M* + 1, 6), 719 [$Pt(PPh_3)_2$, 2], 457 [$Pt(PPh_3)$, 2], 379 [$Pt(PPh_2)$, 3] 307 (PtC_3Ph, 17), 154 (Ph_2, 100) and 77 (Ph, 49%). Decomposition point 160 °C.

(3-Methyl-3-phenylcyclopropene)bis(triphenylphosphine)-platinum. The preparation was similar to that of [$Pt(3,3\text{-}Ph_2C_3H_2)(PPh_3)_2$] except that [$Pt(C_2H_4)(PPh_3)_2$] (0.46 g, 0.62 mmol) and 3-methyl-3-phenylcyclopropene (0.12 g, 0.92 mmol) were used, yield 0.33 g (63%). ^{1}H NMR ($CDCl_3$): δ 1.91 (t, 3 H, $^4J_{PtH}$ = 6.96, CH_3), 2.90 (tt, 2 H, $^2J_{PtH}$ = 19.7, $^3J_{PH}$ = 7.25, CH=CH) and 7.08–7.40 (m, 35 H, C_6H_5). Decomposition point 130–140 °C.

(3,3-Dimethylcyclopropene)bis(triphenylphosphine)platinum.[11] The preparation was similar to that of [$Pt(3,3\text{-}Ph_2C_3H_2)(PPh_3)_2$] except that [$Pt(C_2H_4)(PPh_3)_2$] (1.46 g, 1.95 mmol) and 3,3-dimethylcyclopropene (0.26 g, 3.82 mmol) were used, yield 1.39 g (90%). ^{1}H NMR ($CDCl_3$): δ 1.45 (s, 3 H, $^4J_{PtH}$ = 0, CH_3 *anti*), 1.97 (t, 3 H, $^4J_{PtH}$ = 4.2, CH_3 *syn*), 3.06 (tt, 2 H, $^2J_{PtH}$ = 14.0, $^3J_{PH}$ = 7.0, CH=CH) and 6.8–7.6 (m, 30 H, C_6H_5) (Found: C, 62.7; H, 4.7. $C_{41}H_{38}P_2Pt$ requires: C, 62.4; H, 4.9%).

Cyclopropenebis(triphenylphosphine)platinum.[11] The preparation of [$Pt(C_3H_4)(PPh_3)_2$] was carried out in an analogous manner to the preparation of [$Pt(3,3\text{-}Ph_2C_3H_2)(PPh_3)_2$], from [$Pt(C_2H_4)(PPh_3)_2$] (0.40 g, 0.53 mmol) except the reaction vessel was cooled initially in liquid nitrogen. More than 1.5 equivalents of cyclopropene were added to the closed system under a slight vacuum *via* tubing connected to the vial containing cyclopropene, which was stored at liquid nitrogen temperature. This vessel was allowed to warm slowly from −196 °C until the cyclopropene began to distil over. After complexation the cyclopropene complex formed was as stable as any of the disubstituted cyclopropene complexes and was isolated in the same manner, yield 0.25 g (62%). ^{1}H NMR (CD_2Cl_2): δ 2.03 (t, 1 H, $^3J_{PtH}$ = 116.8, H_{syn}) 2.31 (t, 1 H, $^3J_{PtH}$ = 232.5, H_{anti}), 2.94 (m, 2 H, CH=CH) and 7.1–7.4 (m, 30 H, C_6H_5). ^{195}Pt NMR (toluene–[$^2H_8$]toluene): δ −5200 (tdd, $^1J_{PtP}$ = 3375, $^3J_{PtH_{syn}}$ = 116.8, $^3J_{PtH_{anti}}$ = 232.5). Mass spectrometry: *m*/*z* 760 (*M* + 1, 12), 719 [$Pt(PPh_3)_2$, 4], 457 [$Pt(PPh_3)$, 8], 379 [$Pt(PPh_2)$, 5], 302 (PtPPh, 23), 154 (Ph_2, 100) and 77 (Ph, 38%).

(1,2-Diphenylcyclopropene)bis(triphenylphosphine)platinum 2. The preparation of [$Pt(1,2\text{-}Ph_2C_3H_2)(PPh_3)_2$] was similar to that of [$Pt(3,3\text{-}Ph_2C_3H_2)(PPh_3)_2$], from [$Pt(C_2H_4)(PPh_3)_2$] (0.57 g, 0.76 mmol) and 1,2-$Ph_2C_3H_2$ (0.22 g, 1.14 mmol) with recrystallisation from toluene–ethanol, yield 0.37 g (53%). ^{1}H NMR (CD_2Cl_2): δ 2.25 (t, 1 H, $^3J_{PtH}$ = 79.2, H_{syn}), 2.54 (t, 1 H, $^3J_{PtH}$ = 197.6, H_{anti}) and 6.7–7.3 (m, 40 H, C_6H_5). Mass spectrometry: *m*/*z* 912 (*M* + 1, 16), 719 [$Pt(PPh_3)_2$, 4], 457 [$Pt(PPh_3)$, 6], 379 [$Pt(PPh_2)$, 6], 307 (PtC_3Ph, 17), 154 (Ph_2, 100) and 77 (Ph, 50%). Decomposition point 151–153 °C.

(1,2-Di-*n*-butylcyclopropene)bis(triphenylphosphine)platinum. The preparation of [$Pt(1,2\text{-}Bu_2C_3H_2)(PPh_3)_2$] was carried out in a similar manner to that of [$Pt(1,2\text{-}Ph_2C_3H_2)(PPh_3)_2$] using [$Pt(C_2H_4)(PPh_3)_2$] (0.5 g, 0.67 mmol) and 1,2-dibutylcyclopropene (0.15 g, 0.99 mmol). After 20 min of reaction, ethanol (50 cm^3) was added and then the solution was concentrated to dryness *in vacuo*. The residue was recrystallised from toluene–ether, yield 0.21 g (36%). ^{1}H NMR ($CDCl_3$): δ 0.53 (m, 6 H, CH_3 of butyl), 0.85–1.0 (m, 8 H, CH_2CH_2 of butyl), 1.7 (m, 2 H, CH_2) and 2.4 (m, 4 H, α-CH_2 of butyl). Decomposition point 118–122 °C.

(1-*n*-Butyl-2-trimethylsilylcyclopropene)bis(triphenylphosphine)platinum. The preparation of [$Pt\{1\text{-}Bu\text{-}2\text{-}(Me_3Si)C_3H_2\}(PPh_3)_2$] was carried out using [$Pt(C_2H_4)(PPh_3)_2$] (0.24 g, 0.32 mmol) and 1-butyl-2-trimethylsilylcyclopropene (0.08 g, 0.49 mmol) in an analogous manner to that described for [$Pt(3,3\text{-}Ph_2C_3H_2)(PPh_3)_2$]. ^{1}H NMR ($CD_2Cl_2$): δ −0.42 (s, 9 H, $SiMe_3$), 0.56 (t, 3 H, CH_3 of butyl), 0.70 (s, 2 H, CH_2), 1.27–1.45 (m, 4 H, CH_2CH_2 of butyl) and 2.5 (t, 2 H, α-CH_2 of butyl). Mass spectrometry: *m*/*z* 888 (M^+, 93), 811 (*M* − Ph, 2), 719 [$Pt(PPh_3)_2$, 26], 530 [$Pt(PPh_3)(SiMe_3)$, 22], 457 [$Pt(PPh_3)$, 16], 379 [$Pt(PPh_2)$, 27], 302 [Pt(PPh), 25], 136 (65) and 73 ($SiMe_3$, 100%).

(3,3-Dimethylcyclopropene)[1,2-bis(diphenylphosphino)-ethane]platinum. The olefin complex [$Pt(C_2H_4)$(dppe)] was made *in situ* by dissolving [$PtCl_2$(dppe)] (0.20 g, 0.3 mmol) in degassed thf (40 cm^3) and bubbling through ethene in the presence of sodium naphthalene (4 cm^3, 0.2 mol dm^{-3} in thf) for 30 min.[14] A ^{31}P NMR spectrum showed the presence of only the ethene complex (δ 54.85, $^1J_{PtP}$ = 3305 Hz). The reaction mixture was cooled to −50 °C and 3,3-dimethylcyclopropene (0.025 g, 0.37 mmol) added quickly *via* a syringe. The mixture was then allowed to return to room temperature and taken to dryness. The residue was dissolved in hexane and the insoluble impurity filtered off, leaving a pale yellow solution. The solution was taken to dryness yielding the product as a light yellow powder.

(3,3-Diphenylcyclopropene)[1,2-bis(diphenylphosphino)-ethane]platinum. To [$Pt(C_2H_4)$(dppe)] (0.37 mmol) made *in situ* from [$PtCl_2$(dppe)] (0.28 g, 0.42 mmol) as above 3,3-diphenylcyclopropene (0.11 g, 0.57 mmol) was added and the reaction mixture stirred for 15 min. The thf was removed *in vacuo* leaving a brown oily residue which was dissolved in thf–dichloromethane (4:1, 4 cm^3). Hexane (100 cm^3) precipitated the product as a light brown powder which was filtered off and dried, yield 0.15 g (52%).

(3-Methyl-3-phenylchloropropene)[1,2-bis(diphenylphosphino)ethane]platinum. This preparation was carried out as that with 3,3-diphenylcyclopropene. The substituted cyclopropene (0.074 g, 0.57 mmol) was added to *ca.* 0.37 mmol of the ethene complex. Further product was recovered from the crystallisation mother-liquor after a few days at −20 °C. Recrystallisation using toluene–ethanol gave a yellow product, yield 0.11 g (41%).

(1,2-Diphenylcyclopropene)[1,2-bis(diphenylphosphino)-ethane]platinum. This was prepared similarly from the ethene complex (0.37 mmol) and 1,2-diphenylcyclopropene (0.50

mmol). The desired product is slightly soluble in hexane, so the solution was concentrated and cooled on a methylated spirit slug bath to promote precipitation. A second crop was formed from the mother-liquor stored at −20 °C.

(1,2-Dibutylcyclopropene)[1,2-bis(diphenylphosphino)-ethane]platinum. This reaction was carried out on the same scale and in the same manner as the reaction of [Pt(C_2H_4)-(dppe)] with 1,2-diphenylcyclopropene.

(1-Butyl-2-trimethylsilylcyclopropene)[1,2-bis(diphenylphosphino)ethane]platinum. This reaction was carried on the same scale and in the same manner as the reaction of [Pt(C_2H_4)-(dppe)] with 1,2-diphenylcyclopropene.

Reaction of 3-chloromethyl-1,2-dichloro-3-methylcyclopropene with (ethene)bis(triphenylphosphine)platinum. To [Pt(C_2H_4)-(PPh_3)$_2$] (0.37 g, 0.5 mmol) dissolved in degassed toluene (10 cm^3) was added neat tetrasubstituted cyclopropene (0.13 g, 0.67 mmol). The solution was stirred for 1 h with slight warming. Ethanol (degassed) (100 cm^3) was added and the flask cooled. The solution was then concentrated until precipitation occurred. The white precipitate was collected by filtration and dried *in vacuo*, yield 0.21 g (47%). ^{1}H NMR (CD_2Cl_2): δ 1.51 (dd, 3 H, CH_3), 4.44 (dq, 1 H, $^2J_{HH}$ = 2.3, $^4J_{HH}$ = 1.1, CH_2Cl), 4.81 (dq, 1 H, $^4J_{HH}$ = 1.47, CH_2Cl) and 7.13–7.67 (m, 60 H, C_6H_5). ^{31}P NMR ($CDCl_3$): δ 13.97 (dt, $^1J_{PtP}$ = 4250) and 16.15 (dt, $^1J_{PtP}$ = 1942, $^2J_{PP}$ = 16 Hz). ^{13}C NMR ($CDCl_3$): δ 20.94 (s, CH_3), 77.20 (s, CH_2Cl), 116.92 (s, quaternary C), 131.33 (s, ring CCl), 127.0–135.0 (36C, C_6H_5) and 142.22 (s, α-C). ^{195}Pt NMR ($CHCl_3$–$CDCl_3$): δ −4432.7 (dd). Mass spectrometry: *m*/*z* 892 (*M* + 2, 18), 854 (*M* − Cl, 5), 790 [Pt(C_3Cl)(PPh_3)$_2$, 11], 755 [Pt(C_3)(PPh_3)$_2$, 12], 719 [Pt(PPh_3)$_2$, 78], 577 (*M* − PPh_3 − Me, 6), 297 (*M* − Cl_2 − PPh, 212), 262 (PPh_3, 100) and 185 (PPh_2, 84%).

Reaction of 1,2,3-tri-*tert*-butylcyclopropene with (ethene)bis-(triphenylphosphine)platinum. This reaction was carried out in an analogous manner to the preparation of [Pt(3,3-$Ph_2C_3H_2$)-(PPh_3)$_2$] but reaction time was 1 h. After work-up in the usual manner only starting material was isolated, as shown by ^{31}P NMR spectroscopy. The organic material was also isolated unchanged. No reaction had occurred.

Crystal structure analysis of [Pt(3,3-$C_3H_2Ph_2$)(PPh_3)$_2$]·C_6H_5Me 1

Crystal data. $C_{51}H_{42}P_2Pt·C_7H_8$, *M* = 1004.1, triclinic, space-group *P*$\bar{1}$ (no. 2), *a* = 15.662(1), *b* = 15.370(1), *c* = 11.1666(7) Å, α = 80.521(6), β = 117.842(6), γ = 88.357(7)°, *U* = 2327.2(3) $Å^3$, *Z* = 2, D_c = 1.432 g cm^{-3}, *F*(000) = 1012, μ(Mo-Kα) = 31.5 cm^{-1}, λ(Mo-Kα) = 0.710 69 Å.

Slow diffusion of layered degassed ethanol over a solution of [Pt(3,3-$C_3H_2Ph_2$)(PPh_3)$_2$] in toluene at −20 °C produced colourless needle-like crystals which were air-stable for a short period. Several of these crystals were selected and mounted on fine glass fibres in air. Oscillation and Weissenberg photographs showed excellent diffraction patterns and one crystal of dimensions 0.11 × 0.13 × 1.0 mm was selected for data collection at room temperature on an Enraf-Nonius CAD4 diffractometer with monochromated Mo radiation. Accurate cell dimensions were determined using the 13 strongest independent reflections with θ between 12 and 13°, giving a total of 25 reflections including symmetry equivalents, each measured four times with different orientations of the reflection plane. For the structure analysis, a total of 4314 unique reflections, of which 3478 had $I > 2\sigma_I$, were measured to θ_{max} = 20°. Absorption, Lorentz-polarisation and deterioration corrections were applied. The structure was solved by using the heavy-atom method in the SHELX program.[31] From the Patterson map the Pt coordinates were determined. The C and P atoms were located from Fourier and Fourier-difference maps.

Refinement (on *F*) was by large-block-matrix least-squares methods in SHELXN.[31] All of the non-hydrogen atoms were refined anisotropically. The two hydrogen atoms on the cyclopropene ring were located in a Fourier-difference map and refined satisfactorily with minimal geometric constraints [C–H 0.98(1) Å] and three isotropic thermal parameters. The hydrogens on all the phenyl rings were placed in idealised positions and their thermal parameters U_{iso} allowed to ride with the parent carbon atom. The final refinement resulted in an *R* factor of 0.053 and a weighted *R* factor *R*′[31] of 0.042 for all data weighted $w = (\sigma_F^2 + 0.000\,52F^2)^{-1}$. In the final difference map, the only peaks above the background noise are *ca.* 0.75 e $Å^{-3}$ and are close to the Pt atom.

Crystal structure analysis of [Pt(1,2-$C_3H_2Ph_2$)(PPh_3)$_2$] 2

Crystal data. $C_{51}H_{42}P_2Pt$, *M* = 911.9, monoclinic, space group $P2_1/a$ (equivalent to no. 14), *a* = 20.577(11), *b* = 10.142(7), *c* = 21.883(13) Å, β = 117.12(5)°, *U* = 4065(5) $Å^3$, *Z* = 4, D_c = 1.490 g cm^{-3}, *F*(000) = 1824, μ(Mo-Kα) = 36.0 cm^{-1}, λ(Mo-Kα) = 0.710 69 Å.

Slow diffusion of layered degassed ethanol over a solution of [Pt(1,2-$C_3H_2Ph_2$)(PPh_3)$_2$] in toluene at −20 °C produced colourless platy crystals which were air-stable for a period of several weeks. One crystal of size *ca.* 0.67 × 0.24 × 0.05 mm was selected and mounted on a fine glass fibre in air. Data were collected at room temperature.

The crystal structure analysis followed a procedure very similar to that described above. 5291 Unique reflections, of which 2896 had $I > 2\sigma_I$, were measured to θ_{max} 22.5°. Refinement was concluded with *R* 0.078 and *R*′[31] 0.082 for 3163 reflections (with $I > 1.5\sigma_I$) weighted $w = (\sigma_F^2 + 0.007\,89F^2)^{-1}$. The final difference map showed peaks at 2.9 and 3.4 e $Å^{-3}$, both close to the Pt atom.

For both analyses, scattering factor curves were taken from ref. 32. Computer programs have been noted above and previously,[33] and were run on a MicroVAX 3600 computer in the Nitrogen Fixation Laboratory.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc.*, *Dalton Trans.*, 1997. Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/422.

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